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<b>(54) Title:</b> DELIGNIFICATION OF CHEMICAL PULP WITH PEROXIDE IN THE PRESENCE OF TRANSITION METAL  <b>(57) Abstract</b>  The invention relates to a process for the delignification of a chemical pulp, such as a sulfate or sulfite pulp, in which process the pulp is treated with a peroxide and/or a peracid in the presence of an activating Ti-, V- or Cr-group transition metal, such as molybdenum, vanadium or tungsten. The essential idea in the invention is that, before this peroxide and/or peracid treatment, heavy metals derived from the wood raw material, such as iron, manganese and/or copper, are removed from the pulp by chelation. In the chelation the heavy metals are converted to soluble complex salts which are removed along with the chelating solution or washing water. The chelation and the peroxide and/or peracid treatment constitute parts of a bleaching sequence which contains as possible other treatment steps, for example, a treatment with oxygen, a second chelation step, and an alkaline peroxide treatment.		

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Delignification of chemical pulp with peroxide in the presence of transition metal.

The present invention relates to a process for the delignification of a chemical pulp, in which process the pulp is treated with a peroxide or a peracid in the presence of an activating Ti-, V- or Cr-group transition metal. The said transition metals include Mo, V, Nb, Ta, Ti, Zr, Hf and W.

After the cooking, chemical pulp is brown, owing to residual lignin present in it. The pulp to be used for higher-grade papers is bleached after cooking in order to remove the lignin.

The bleaching chemical used has conventionally been chlorine, by means of which an effective bleaching is achieved and the quality of the paper obtained is high. However, owing to the environmental problems caused by chlorine, there has recently been to an increasing degree a shift to other bleaching chemicals, such as chlorine dioxide, oxygen, ozone, peroxides, and peracids. The overall objective has been to shift to bleaching which is completely free of chlorine chemicals in order to avoid the environmental hazards caused by chlorine chemicals, and chlorine residues in completed paper.

The bleaching process usually comprises a bleaching sequence made up of successive treatment steps, wherein oxidative steps which decompose lignin and alkaline washing steps alternate. By bleaching without chlorine chemicals, wherein the oxidants used are oxygen and alkaline peroxide, usually a pulp has been obtained which in its brightness, 83-87 % ISO, and in its strength is not of the level of pulp bleached with chlorine chemicals. When ozone has been used as the oxidant, a brightness above 88 % ISO has been achieved, but there has been the problem of the proneness of the process to disturbances. Thus there has been a need to find a system by means of which, without the use of chlorine chemicals, a fully bleached pulp

stronger than previously and corresponding in quality to conventional pulps bleached with chlorine chemicals could be obtained through a process reliable in operation.

It is known that the delignification of chemical pulps can be promoted by treating the pulp with hydrogen peroxide in the presence of certain metals, such as Sn, Ti, V, W, Mo, Cr, Nb, Os and Se, or compounds thereof (1, 2, 3, 4, 5, 6, 7, 8).

Metal compounds which have been used in organic chemistry to activate hydrogen peroxide are listed in, for example, the book Catalytic Oxidations with Hydrogen Peroxide as Oxidant (G. Strukul, Kluwer Academic Publishers 1992), Chapter 1, "Introduction and Activation Principles," page 9.

In the said references, the above-mentioned metallic activators have been used mainly in the peroxide step after the cooking or after the oxygen step.

A chemical pulp contains, in a water-insoluble form, heavy metals derived from the wood raw material, mainly iron, manganese and copper, which catalyze the decomposition of the peroxide and the peracid used as oxidants and thereby increase the consumption of these chemicals in bleaching. These decomposition reactions also have a detrimental effect on the quality of pulp obtained by peroxide bleaching.

According to the invention it has now been observed, surprisingly, that by removing the said wood-derived heavy metals before metal-activated (e.g. Mo, W, V) peroxide delignification, the efficiency of the delignification step can be improved in many ways. When the detrimental heavy-metal ions have been eliminated, the detrimental decomposition of peroxide is reduced. In addition, by the removal of detrimental heavy metals before the delignification step, the potential for concentration of the wood-derived heavy metals in the cycle of the

activator metal in peracid and/or peroxide delignification in industrial conditions is avoided.

It is an object of the invention thus to decrease the detrimental effect of heavy metals and to increase the efficacy of the peroxide and/or peracid treatment, activated with molybdenum or other such metal, in such a manner that the consumption of the said chemicals decreases and the quality of the obtained bleached pulp is improved. The invention is characterized in that, before a peroxide and/or peracid treatment activated with an above-mentioned transition metal, the pulp is chelated in order to eliminate any heavy metals, such as iron, manganese and/or copper, derived from the wood raw material.

Optimally the chelation takes place directly before the activated delignification step, whereby the situation is avoided that heavy metals released in the bleaching step/steps between the removal of heavy metals and the activated delignification would pass into the activated peroxide and/or peracid step.

In the chelating step a chemical is used which forms water-soluble complex salts with the heavy-metal ions to be removed. On the basis of experiments performed, it is possible by the bleaching according to the invention, comprising chelating and an activated peroxide and/or peracid treatment, to obtain, without chlorine chemicals, a strong, completely white pulp with a brightness above 88 % ISO.

Compared with the bleachings of chemical pulps, referred to above (ref. 1, 2, 3, 4, 5, and 6), a considerably better end result is achieved by means of the present invention. The removal of detrimental heavy metals before metal-activated delignification has led to an improved end result.

The bleaching can be performed without chlorine chemicals or ozone, although the chelating according to the invention, pre-

ceding the peroxide and/or peracid step, is also advantageous in a bleaching sequence which comprises chlorine chemical or ozone treatment steps. The invention decreases the consumption of peroxide and/or peracid and enables the metal used as an activator to be efficiently recycled. The invention is suitable for all different chemical pulps, such as softwood and hardwood sulfate pulps, sulfite pulps, semialkaline pulps, and organosolv pulps. Furthermore, the invention can be exploited in pulping processes, in particular organosolv cooking, such as milox.

According to one preferred embodiment of the invention, chelation constitutes a treatment step directly preceding the activated peroxide and/or peracid treatment. The chelation can, for example, be performed within an acid pH range before the peroxide and/or peracid treatment, the pH of which is within the range 2-7, preferably 4.5-5.5, and temperature within the range 30-120 °C, preferably approx. 80-100 °C. The advantage here is that it is not necessary to adjust the pH of the pulp between the successive treatment steps in the sequence. On the other hand, the pH of the chelating step is not in itself critical, and, when necessary, it can be adjusted by means of, for example, sulfuric acid, sulfur oxide, or organic acids.

According to another embodiment of the invention, the pulp is subjected to two chelating treatments, in which case the treatment steps succeed one another in the bleaching sequence, in the following order: chelation, activated peroxide and/or peracid treatment, chelation and alkaline peroxide treatment. The second chelating step removes from the pulp any residual activator metal, such as molybdenum, the presence of which in the alkaline peroxide treatment step would be detrimental. The chelation at the same time removes any heavy-metal residues possibly detached from the pulp by the activated peroxide or peracid delignification.

The chelating chemical may be DTPA (diethylenetriaminepentaacetic acid), which can be used in the form of a commercial 40 % Na salt solution. A suitable amount of the chemical is 0.5-5 kg of DTPA calculated as 100 % chemical per one metric ton of pulp. The acting time of the chelating chemical may be, for example, 15 min - 4 h and the temperature 30-120 °C, preferably 40-90 °C. DTPA was used with good results in the embodiment examples described below. However, according to the invention also other known chelate-forming substances can be used, such as EDTA (ethylenediaminetetraacetic acid), several organic acids, phosphonic acid derivatives such as DTMPA, 8-hydroxyquinoline, ammoniumthiocyanate, quaternary ammonium compounds, etc.

In the said activated peroxide and/or peracid treatment, when used alone peracid gives a better delignification result than does peroxide. It is, however, optimal to use both peroxide and peracid simultaneously. A suitable peroxide is hydrogen peroxide, and especially suitable peracids include peracetic acid and performic acid.

The metal used as the activator in the peroxide and/or peracid step is preferably molybdenum, which can be used as a suitable compound, for example as a Na molybdenate solution, which is fed into the pulp separate from the feed of the peroxide and/or peracid. In the preliminary experiments, vanadium and tungsten were used in addition to molybdenum, with good results. It is, however, clear that any transition metals of the above-mentioned groups, known per se, which activate peroxide or peracid delignification, can be used in the invention.

In addition to the activator metal, also silicon and/or phosphorus compounds may be used as additives promoting peroxide or peracid delignification. It is thus possible to feed into the pulp, for example, sodium silicate and/or sodium phosphate in the same solution as molybdenum or other such activator metal.

The silica or phosphorus may also belong to the same compound as the activator metal, one example being compounds of the silicomolybdenic acid type.

It is further possible to use in the activated peroxide and/or peracid treatment other additives, depending on the conditions, such as acetic acid or other organic acids, which serve as a buffer to maintain the pH at the optimum level, as well as elements B, Ni, Co, Cr and Se or periodic acid, which in some cases increase the reactivity of the chemical combinations used.

The following embodiment examples include experiment series in which the effect of the various parameters of bleaching on the results obtained was investigated.

#### Example 1

An investigation was made of the effect of chelation by means of DTPA on the bleaching results of a subsequent activated peroxide step with different concentrations of different heavy metals in the initial material, i.e. acid-delignified softwood sulfate pulp. The results are given in accompanying Table 1.



Table 1

Experiment No.	1	2	3	4	5	6	7	8
<b>Chelation pretreatment</b>								
DTPA, kg/t	-	-	2	-	2	2	-	2
Fe, ppm	5.9	5.9	3.9	5.9	3.9	3.9	18	3.2
Mn, ppm	38	38	0.26	38	0.26	0.26	87	0.4
<b>Delignification</b>								
Temperature, °C	90	90	90	100	100	100	90	90
Time, min	210	210	210	210	210	210	210	210
Consistency, %	10	10	10	10	10	10	10	10
H <sub>2</sub> O <sub>2</sub> , kg/t	20	20	20	20	20	20	20	20
Mo, kg/t	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Si/Mo, mol/mol	1/12	1/12	1/12	1/12	1/12	1/12	1/12	1/12
DTPA, kg/t	-	2	-	2	-	2	2	-
pH, initial	4.5	4.5	4.5	5.3	5.3	5.3	5.3	5.3
pH, final	3.8	4.0	3.9	4.5	4.3	4.3	4.3	4.3
Residual H <sub>2</sub> O <sub>2</sub> , kg/t	2.8	3.6	8.8	0	4.5	5.4	0	8.5
Kappa number	8.6	8.9	8.0	6.7	6.2	6.2		8.2
Viscosity, dm <sup>3</sup> /kg	864	876	867	803	807	817	838	892
Brightness, % ISO	40.3	40.0	40.8	46.4	46.3	45.1	39.1	40.0

Experiments Nos. 1-6: O-delignified softwood sulfate pulp:  
Kappa 17.3, viscosity 978 dm<sup>3</sup>/kg, 38.5 % ISO

Experiments Nos. 7-8: O-delignified softwood sulfate pulp:  
Kappa 18.2, viscosity 990 dm<sup>3</sup>/kg, 37.9 % ISO

Experiments 3, 5, 6 and 8: Chelate treated (DTPA) and washed  
before the activated peroxide step

As shown in the table, the removal of the heavy-metal ions is of quite crucial importance in terms of the selective delignification (kappa/viscosity) and peroxide consumption in the activation step.

Experiments 1 and 2 were performed on unchelated softwood sulfate pulp after an oxygen step, and Experiment 3, respectively, on chelate-treated and washed pulp. Experiment 3 consumed considerably more peroxide than did Experiment 1 or 2. Said activated peroxide steps were performed at 90 °C. An activated peroxide step at 100 °C yielded similar results. An activated peroxide step (mP) after a chelating step consumed considerably less peroxide and gave a more selective delignification than did a corresponding activated step before which chelate treatment and wash had not been carried out (compare Experiments 4 and 5 or 4 and 6).

In Experiments 1-6, an oxygen-delignified softwood sulfate pulp was used the heavy metal content of which was quite low. After the cooking and/or an oxygen step a sulfate pulp may, however, have considerably higher heavy-metal concentrations. Especially a hardwood sulfate pulp may have heavy-metal concentrations considerably higher than those shown in the table.

The low metal amounts in Experiments 3, 5, 6 and 8 are probably inside the fiber and are thus not effective during the reaction; during delignification, however, metals are released from the fiber.

In Experiments 7 and 8, the raw material used was a softwood sulfate pulp in which the Fe and Mn concentrations after oxygen delignification were 18 ppm Fe and 87 ppm Mn. An activated peroxide step without a preceding chelate treatment and wash consumed the entire portion of 20 kg H<sub>2</sub>O<sub>2</sub>/t, whereas an mP step after a chelate treatment and a wash consumed peroxide in an amount of 11.5 kg H<sub>2</sub>O<sub>2</sub>/t. Also, the selectivity of the deligni-

fication of the activated peroxide step (Experiment No. 8) was considerably higher than that of the reference (Experiment No. 7).

The reason for the higher consumption of peroxide and the lower selectivity was heavy metals, which decompose peroxide, causing non-desirable reactions and at the same time reducing the number of desirable reactions. High temperatures (above 80 °C) are optimal in terms of the efficacy of activated peroxide delignification. On the other hand, the catalyzing effect of heavy metals (Mn, Fe, Cu, ...) on the decomposition of peroxide also intensifies when the temperature rises. When the said detrimental concentrations of heavy-metal ions have been removed before the activated peroxide/peracid delignification step, an effective and selective delignification is achieved, since peroxide is not consumed in decomposition reactions, catalyzed by heavy-metal ions and unnecessarily consuming peroxide and weakening the selectivity of the delignification.

#### Example 2

A softwood sulfate pulp was subjected to chelation, an oxygen step and a second chelating step by using 1 kg of DTPA/one metric ton of pulp. The kappa number of the obtained pulp was 7.7, brightness 55.8 % ISO, and viscosity 800 dm<sup>3</sup>/kg. Thereafter, delignification was carried out, the results of which are shown in accompanying Table 2.

Table 2

Exp. No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Time, min	200	200	400	400	400	400	200	400	200	200	200	200	200
Temperature, °C	90	90	90	90	90	90	90	90	90	100	100	100	90
Consistency, %	12	12	12	12	12	12	12	12	12	12	12	12	12
H <sub>2</sub> O <sub>2</sub> , kg/t	15	8.85	8.85 + 4.4	15 + 7.5	8.85 + 4.4	15 + 7.5	15	15 + 7.5	8.85	8.85	15	15	8.85
Mo, kg/t	0.33	0.33	0.33	0.33	-	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
Si, 10 <sup>-3</sup> kg/t	-	-	-	-	-	27.5	27.5	-	27.5	27.5	27.5	-	27.5
P, kg/t	-	-	-	-	-	-	-	0.33	-	-	-	-	-
Peracetic acid, kg/t	-	6.15	6.15 + 3.3	-	6.15 + 3.3	-	-	-	6.15	6.15	-	-	-
Performic acid, kg/t	-	-	-	-	-	-	-	-	-	-	-	-	6.15
pH initial	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
pH final	4.4	4.7	5.2	4.7	5.1	5.1	4.7	5.2	4.9	4.9	4.7	4.6	4.6
Residual H <sub>2</sub> O <sub>2</sub> , kg/t	8.5	3.9	6.2	15.2	9.6	12.7	8.8	11.5	4.3	2.3	6.8	7.2	4.9
Kappa	3.6	3.2	2.4	2.9	3.9	2.6	3.4	2.7	3.1	2.3	2.7	2.9	3.6
Brightness, % ISO	64.9	67.1	73.7	69.1	71.3	71.5	66.1	71.5	68.0	70.3	68.4	67.0	64.6
Viscosity, dm <sup>3</sup> /kg	758	748	748	758	752	751	768	748	771	710	726	730	741

In Experiments 3, 4, 5, 6 and 8, some of the chemicals were added after 200 min, in connection with pH control (pH 5.2).

Molybdenum-activated peracetic acid/peroxide delignification gives a better final result than does molybdenum-activated peroxide delignification, as shown by a comparison of Experiments 1 and 2 in Table 3. Silicate-modified molybdenum-activated peracetic acid/peroxide delignification (Experiment No. 9) gives an even better result than do those mentioned above.

The use of phosphorus instead of silicate gives a result almost equally good, as shown by a comparison of Experiments 6 and 8.

Raising of the temperature increases the efficacy of silicate-modified molybdenum-activated peracetic acid/peroxide delignification (compare Experiments 9 and 10). A raising of the temperature and/or an increasing of the reaction time also intensifies the other delignification processes concerned, as shown by a comparison of Experiments 11 and 12, as well as 1.

Peracetic acid/peroxide delignification (Experiment No. 5) gives a poorer result than does molybdenum-activated peracetic acid/peroxide delignification (Experiment No. 3).

### Example 3

A softwood sulfate pulp was subjected to oxygen delignification, a chelating step by using 1 kg of DTPA/metric ton of pulp, and an alkaline oxygen-promoted peroxide delignification. The kappa number of the obtained pulp was 9.7, brightness 65.0 % ISO, viscosity 837 dm<sup>3</sup>/kg. The results of the subsequent delignification are shown in the following Table 3.

Table 3

Exp. No.	1	2	3	4	5	6	7	8	9	10	11	12
Time, min	200	200	200	200	200	200	200	120	360	200	200	200
Temperature, °C	80	80	80	60	80	105	80	80	80	80	90	80
Consistency, %	10	10	10	10	10	10	10	10	10	20	20	10
H <sub>2</sub> O <sub>2</sub> , kg/t	20	20	20	20	20	20	20	20	20	20	20	20
Mo, kg/t	2	2	2	1	1	1	0.5	1	1	1	1	-
pH initial	2.5	5.2	7.5	5.2	5.2	5.2	5.2	5.7	5.2	5.3	5.1	5.2
pH final	2.5	4.4	5.4	5.2	4.6	4.2	4.5	5.3	4.4	4.6	4.4	5.0
Residual H <sub>2</sub> O <sub>2</sub> , kg/t	7.5	7.4	0	14.6	7.9	3.7	9.5	9.4	8.1	4.5	2.9	17.8
Kappa	3.1	3.4	4.6	6.5	4.1	2.2	4.5	5.3	3.1	3.2	2.9	9.1
Brightness, % ISO	68.4	70.9	65.8	67.6	68.5	73.9	68.5	68.7	71.0	72.9	73.3	67.2
Viscosity, dm <sup>3</sup> /kg	691	797	794	831	827	674	804	822	791	802	757	835
Si/Mo ratio 1/12 constant												

The pulp obtained in Experiment 11 was subsequently subjected to an alkaline peroxide treatment by using H<sub>2</sub>O<sub>2</sub> at a rate of 20 kg /metric ton at 80 °C for 240 min, the initial pH being 10.6, without a preceding chelating step (Experiments 111 and 112), and with a preceding chelating step (2 kg DTPA/t) (Experiment 113) for 30 min at 70 °C, the initial pH being 5.5. The results are shown in the following Table 3a.

Table 3a Results of alkaline peroxide step

Exp. No.	111	112	113
DTPA, kg/t	-	1.5	-
Residual H <sub>2</sub> O <sub>2</sub> , kg/t	1.6	1.2	11.5
Kappa	1.6	1.6	1.7
Brightness, % ISO	86.0	85.8	86.5
Viscosity, dm <sup>3</sup> /kg	686	703	699

Table 3 shows examples of the effect of various reaction conditions on silicomolybdenum-activated peroxide delignification.

Of the pH values tested (Experiments 1, 2 and 3), an initial pH of 5.2 gave clearly the best result. On the basis of experiments, a pH range of approx. 4.4-5.4 is the optimum for selective delignification.

A high temperature (compare Experiments 4, 5 and 6), a high consistency (compare Experiments 5 and 10), and a long reaction time (compare Experiments 8, 5 and 9) improve the efficacy of delignification.

With a peroxide charge of 20 kg/t, the delignification efficacy increases as the silicomolybdenum charge increases, as shown by a comparison of Experiments 7, 5 and 2.

The result after the alkaline peroxide step (EP) subsequent to the activation step was best when the activation step had been performed at an initial pH value of approx. 5.2.

A chelating step following the activation step, before a subsequent alkaline peroxide step, saves peroxide to a considerable degree in the EP step by removing heavy metals released during delignification (compare 111, 112 and 113).

The said chelating step also "washes" away molybdenum of the activation step or corresponding catalyst. Molybdenum present in alkaline peroxide bleaching increases the consumption of peroxide, as can be seen in Table 3b.

Table 3b

Exp. No.	1	2	3	4	5
Mo, kg/t	0	0.025	0.05	0.1	0.3
Residual H <sub>2</sub> O <sub>2</sub> , kg/t	14.1	2.5	1.5	1.0	0.4
Kappa	1.5	1.5	1.5	1.5	1.5
Brightness, % ISO	86.8	85.7	85.1	84.9	83.7
Viscosity, dm <sup>3</sup> /kg	688	694	693	700	672

20 kg H<sub>2</sub>O<sub>2</sub>/t, 0.15 kg DTPA/t, 180 min, 80 °C, CS 12 % constant

Raw material for experiments of Table 3b: O-Q-EOP-Q-mP-Q

bleached softwood

sulfate pulp

Kappa 2.6

Brightness 70, % ISO

Viscosity 731 dm<sup>3</sup>/kg

The optimum reaction conditions (especially the pH) of some of the methods tested, especially of certain activated peracid and peracid/peroxide delignifications, deviate from the above-mentioned optimal reaction conditions of Si-Mo-activated peroxide delignification.

#### Example 4

A softwood sulfate pulp was subjected to peroxide-promoted oxygen delignification and a chelating step by using 2 kg of DTPA/one metric ton of pulp. The kappa number of the obtained pulp was 7.4, brightness 62.2 % ISO, and viscosity 895 dm<sup>3</sup>/kg. The results of delignification steps carried out on this pulp are shown in Table 4.



Table 4

Exp. No.	1	2	3	4	5	6
Time, min	2+2	210	210	210	180	210
Temperature, °C	50	90	90	90	75	90
Consistency, %	12	12	12	12	10	12
H <sub>2</sub> O <sub>2</sub> , kg/t	-	20	11.8	20	-	20
Mo, kg/t	-	0.8	0.5	0.8	-	-
Si, kg/t	-	-	0.042	0.067	-	-
Peracetic acid, kg/t	-	-	8.2	-	-	-
O <sub>3</sub> , kg/t	3+3	-	-	-	-	-
ClO <sub>2</sub> , kg act. Cl/t	-	-	-	-	30	-
pH final	2.9	4.5	4.7	4.9	2.2	10.3
Residual H <sub>2</sub> O <sub>2</sub> , kg/t	-	8.8	7.4	9.6	-	8.3
Kappa	2.8	2.8	2.7	2.6	2.1	4.3
Brightness, % ISO	69.9	67.5	70.2	70.2	70.8	81.3
Viscosity, dm <sup>3</sup> /kg	717	831	848	824	848	802

Pulps 1, 2, 3, 4 and 6 of Table 4 were subsequently subjected to a chelating step and the chloride-oxide delignified pulp No. 5 was subjected to an alkali(E) step. The washed pulps 1, 2, 3, 4 and 6 were further subjected to an alkaline peroxide treatment and respectively pulp 5, after an alkali and washing step, to a chlorine dioxide (D) step. The bleaching experiments of Table 4a were continued on from the experiments correspondingly numbered in Table 4.

Table 4a

Exp. No.	1	2	3	4	5	6
Time, min	210	210	210	210	180	210
Temperature, °C	90	90	90	90	80	90
Consistency, %	12	12	12	12	12	12
H <sub>2</sub> O <sub>2</sub> , kg/t	25	25	25	25	-	25
ClO <sub>2</sub> , kg act. Cl/t	-	-	-	-	15	-
pH final	10.2	10.3	10.3	10.3	4.6	10.3
Residual H <sub>2</sub> O <sub>2</sub> , kg/t	19.2	17.7	17.7	19.4	-	22.6
Residual ClO <sub>2</sub> , kg/t	-	-	-	-	0.3	-
Kappa	1.4	1.5	1.4	1.4	0.6	2.6
Brightness, % ISO	86.9	87.2	88.2	88.1	88.3	86.1
Viscosity, dm <sup>3</sup> /kg	656	759	740	750	786	751

In addition to brightness, strength properties corresponding to those of a chlorine dioxide bleached pulp (No. 5) were obtained for the pulps after alkaline peroxide bleachings which followed activated peroxide and peroxide/peracid delignifications (Nos. 2, 3 and 4): with a tensile index of 70, a tear index of 14 was achieved, which is a strength result about 10 % better than that obtained with a conventional alkaline peroxide-bleached TCF pulp (No. 6).

#### Example 5

A softwood sulfate pulp was subjected to peroxide-promoted oxygen delignification and to a chelating step in which DTPA was used at a rate of 2 kg/one metric ton of pulp. The kappa number of the obtained pulp was 7.7, brightness 55.8 % ISO, and viscosity 800 dm<sup>3</sup>/kg. The results of peroxide and peroxide/-

peracid delignification steps, activated with various metals, performed on this pulp are shown in Table 5.

Table 5

Exp. No.	1	2	3	4	5	6	7	8	9	10	11
Time, min	200	200	200	200	200	200	200	200	200	200	200
Temperature, °C	90	90	90	90	90	90	90	90	90	90	90
Consistency, %	12	12	12	12	12	12	12	12	12	12	12
H <sub>2</sub> O <sub>2</sub> , kg/t	20	20	20	20	20	11.8	11.8	11.8	11.8	20	11.8
Peracetic acid, kg/t	-	-	-	-	-	8.2	8.2	8.2	8.2	-	8.2
Mo, kg/t	0.6	-	-	-	-	-	-	-	-	-	-
W, kg/t	-	0.6	-	0.6	-	0.6	-	0.6	-	-	-
V, kg/t	-	-	0.6	-	0.6	-	0.6	-	0.6	-	-
Si, kg/t	-	-	-	0.05	0.05	-	-	0.05	0.05	-	-
pH final	4.6	4.6	4.6	4.5	4.6	4.4	4.5	4.5	4.5	4.4	4.4
Residual H <sub>2</sub> O <sub>2</sub> , kg/t	10.2	11.5	11.9	11.0	11.1	3.1	3.3	3.1	3.2	17.9	8.6
Kappa	3.0	3.5	3.7	3.3	3.4	.30	3.2	2.9	3.0	6.9	5.2
Brightness, % ISO	67.7	67.3	66.9	68.1	68.0	69.9	69.6	70.7	70.5	61.3	65.2

As can be seen in Table 5, Mo-activated peroxide delignification gives better results than do corresponding W- and V-activated peroxide delignifications (compare Experiments 1, 2 and 3). W- and V-activated peroxide/peracid delignifications give better results than do corresponding peroxide delignifications. An addition of silicate promotes W- and V-activated peroxide and peracid delignifications.

Peroxide and peroxide/peracid delignifications activated with mixtures of Mo, W and V also gave effective results.

Example 6

A softwood sulfate pulp was chelate-treated with different complex formers. Before the treatment, the stock had the following heavy-metal concentrations: Fe 3.8 mg/kg of pulp (ppm), Mn 24 ppm. The copper concentration in the stock was insignificant.

As can be seen in Table 6, iron and manganese were removed effectively in all of the chelate pretreatments tested.

Table 6

Exp. No.	1	2	3	4	5	6	7	8	9	10	11
pH	4.5	4.5	4.5	4.5	4.5	4.5	6	6	6	4.5	4.5
EDTA, kg/t	3	-	-	3	-	-	3	-	-	3	-
DTPA, kg/t	-	3	-	-	3	-	-	3	-	-	3
DTMPA, kg/t	-	-	3	-	-	3	-	-	3	-	-
pH control: SO <sub>2</sub>	-	-	-	-	-	-	-	-	-	*	*
H <sub>2</sub> SO <sub>4</sub>	*	*	*	*	*	*	*	*	*	-	-
Temperature, °C	70	70	70	90	90	90	90	90	90	90	90
Consistency, %	5	5	5	5	5	5	5	5	5	5	5
Time, min	45	45	45	45	45	45	45	45	45	45	45
Fe, ppm	2.6	3.9	3.1	3.3	2.3	2.2	2.4	2.4	2.4	3.1	2.4
Mn, ppm	0.3	0.5	0.4	0.2	0.3	0.3	1.6	1.0	1.1	0.2	0.3

Softwood sulfate pulp before chelation: Kappa 9, viscosity 720 dm<sup>3</sup>/kg, Fe 3.8 mg/kg pulp (ppm), Mn 24 ppm.

For an expert in the art it is clear that the various applications of the invention are not limited to those presented above by way of examples, but may vary within the accompanying claims.

List of references

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Claims

1. A process for the delignification of chemical pulp, in which process the pulp is treated with a peroxide or a peracid in the presence of an activating Ti-, V- or Cr-group transition metal, characterized in that, before the activated peroxide and/or peracid treatment, the pulp is chelated in order to remove any heavy metals, such as Fe, Mn and/or Cu, derived from the wood raw material.
2. A process according to Claim 1, characterized in that the chelation constitutes the treatment step directly preceding the activated peroxide and/or peracid treatment.
3. A process according to Claim 2, characterized in that the chelation is performed within an acid pH range before the peroxide and/or peracid treatment, the pH of which is within the range 2-7, preferably 4.5-5.5, and the temperature within the range 30-120 °C, preferably approx. 80-100 °C.
4. A process according to any of the above claims, characterized in that the activated peroxide and/or peracid treatment is followed by a second chelation step before the subsequent alkaline peroxide treatment.
5. A process according to any of the above claims, characterized in that the chemical of the chelation step is DTPA, EDTA or DTPMA.
6. A process according to any of the above claims, characterized in that the pulp is treated with a peracid in the presence of an activator metal.
7. A process according to Claim 6, characterized in that the pulp is treated with a mixture of peroxide and peracid.

8. A process according to any of the above claims, **characterized** in that the peroxide is hydrogen peroxide and the peracid is peracetic or performic acid.
9. A process according to any of the above claims, **characterized** in that the activator metal is Mo, W or V.
10. A process according to any of the above claims, **characterized** in that silica and/or phosphorus is additionally used in the activated peroxide and/or peracid treatment.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 95/00353

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4427490 A (ROBERT C. ECKERT), 24 January 1984 (24.01.84), claim 1 --	1-3,5-9
Y	US 4661205 A (STEVEN S. OW ET AL), 28 April 1987 (28.04.87), column 7, line 64 - column 8, line 12, claim 1 --	1,10
Y	EP 0578303 A1 (SOLVAY INTEROX), 12 January 1994 (12.01.94), page 4, line 50 - page 5, line 25 --	1-3,5-10
A	US 4410397 A (ARTHUR W. KEMPF), 18 October 1983 (18.10.83) -- -----	1-10

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

28/08/95

International application No.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU-A- 8770482	03/03/83
		CA-A- 1190360	16/07/85
		JP-C- 1586778	19/11/90
		JP-B- 2013069	03/04/90
		JP-A- 58054089	30/03/83
EP-A1- 0578303	12/01/94	NONE	
US-A- 4410397	18/10/83	CA-A- 1110018	06/10/81